PHYSICAL CHEMISTRY PARAMETERS THAT CONTROL PESTICIDE PERSISTENCE AND LEACHING IN WATERSHED SOILS

FINAL REPORT

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1 - Rationale/objective

There is ample evidence that the Great Lakes basin is contaminated with pollutants due to agricultural and industrial activities and municipal discharges. Recent human health, wildlife and laboratory studies lend further support that exposure to persistence toxic substances is the most significant problem facing the Great Lakes region (International Joint Commission, 1994). The 35 million people living around the lakes are being affected by the toxic substances coming from diverse sources such as atrazine and PCB's. Children's ability to learn and adults' ability to reproduce now are in danger more than ever (International Joint Commission, 1994). It would be at least technically possible for most industries to prevent the escape of the toxic chemicals that they must use into the environment. The problem for agriculture is fundamentally different from those of other industries. The protection of crops from pest damage requires the introduction of at least some chemical pesticides directly into the environment. As a consequence, one of the few available strategies for protecting the Great Lakes from agricultural pesticides is to find means by which the delivery of the pesticides from cultivated land into the Great Lakes can be prevented or minimized. This can only be done by developing and using methods for risk assessment and for the management of pesticide applications in the field. For such methods to be effective at tolerable costs, they must be based on a working knowledge of the processes that control the persistence and transport of pesticides in soils. In the present case, this means the soils of the Great Lakes watersheds. The three categories of processes that must be accounted for are the physics of water movement, chemical changes and interactions, and microbiological breakdown.

The Great Lakes Water Quality Program (GLWQP) is an agreement between the Governments of the United States and Canada to "Restore and maintain the chemical, physical and biological integrity of the water of the Great Lakes Basin Ecosystem." The first objective of the project was to produce more realistic and relevant information about the chemical changes and interactions. The second objective was to improve the reliability of the computer simulations by integrating this improved chemical information into computer simulation models that already use information about water movement. The project supported the GLWQP initiative in solving the contamination problem on four points: **(a)** Laboratory test methods that have been developed in the project measure pesticide-soil parameters that control the persistence and transport of the pesticides; **(b)** a multidisciplinary computer model has been developed in collaboration with Professor S. O. Prasher, a hydrology engineer as an improved technology for risk assessment and for the control of field operations (Clemente and Prasher, 1993). The project developed a new technology by which contaminant species concentrations can be determined at greater accuracy.This will decrease the pesticide load on the Great Lakes watershed; **(c)**

a pesticide-soil interactions mechanism data base has been created, to support the computerized risk assessment and the computer control of field operations; **(d)** the project has supported two other Great Lakes projects. They are the Microbiological Pathways project and the Sediments project; and **(e)** the project has trained post doctoral fellows, a graduate student, and technicians in an environmental chemistry project.

Because the types of empirical data that are currently used as chemical input for hydrology computer models and risk assessment do not account for cause and effect relationships, they do not support predictive calculations very effectively. There is a need for predicative calculation to assess the contamination problem properly. The objectives of the project are to: a) investigate the fundamental processes of the interactions of soils with contaminants; b) use the predictive physical chemistry constants as input for hydrology computer models to improve prediction of contaminant persistence and fate in the environment under field conditions; c) develop new analytical test methods to determine bioavailable concentrations for risk and hazard assessment, and provides information about chemical speciation of the contaminants in the environment; and d) train qualified scientific people meeting high academic professional standards in a combination of environmental disciplines.

Background

There are many studies on atrazine interactions with the soil, ranging from field experiments (Bowman, 1989; Graham et al., 1992) to laboratory experiments (Bailey et al., 1968; Weber et al., 1969; Weber, 1970; Karickhoff and Morris, 1985; Gamble and Khan, 1992). Gamble and Khan (1990) have demonstrated that the reverse phase High Performance Liquid Chromatography-Microfiltration Technique (HPLC-MFT) can be used to track over time labile and non-labile concentrations, as well as other chemical species of the analyte. The labile surface sorption is the uptake process that leaves some of the pesticide on sorption sites from which it can be quickly recovered back into solution. It can be distinguished experimentally from the uptake processes that produce a type of bound residue. These bound residues are physically trapped so that quick removal is prevented, although slow release can subsequently occur.

Sorption of atrazine. Atrazine is frequently applied to moderately dry soil in a low volume of water. Under such conditions, one expects a rapid wetting of soil aggregates by water molecules (mass flow) which transport atrazine molecules with them to soil particles surfaces. Within a short time small concentrations of surface-sorbed atrazine might develop on soil particles surfaces. This may result in psticide molecules being retained by soil particles as water proceeds in the soil. The movement of the sorbed atrazine molecules is then determined by forces of interactions between the soil and atrazine. The phenomenon of atrazine-soil interactions resembles that seen in the thin layer chromatography in which organic compounds are separated according to their differential movements through a porous media under the influence of a moving solvent. After the sorbed water reaches some sort of distribution equilibrium, there will be a redistribution of atrazine molecules over the soil particles surfaces, and sorption-desorption processes become effective.

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The sorption may be regarded as occurring in three steps, diffusion of the free atrazine molecules from aqueous solution to soil particles, adsorption onto the surface, and diffusion into the interiors of the soil particles. Many authors have reported that the initial adsorption is followed by a second stage that is relatively slower. The pesticide taken up by this second process cannot be recovered by a quick extraction (Talbert, 1965; Mill, 1980; Macalady and Wolfe, 1984; Karickhoff and Morris, 1985). Hamaker et al. (1966) have suggested that organic chemicals slowly diffuse into the interiors of the soil particles. The surface adsorption and diffusion into the bulk of the soil particles can be distinguished experimentally by the HPLC-MFT. The method is based on exhaustive extraction of the pesticide from the soil by the mobile phase, inside the pressurized liquid system of the instrument. That portion of the pesticide that cannot be extracted by the mobile phase is a type of bound residue. The experimental evidence indicates that it is trapped by retarded intraparticle diffusion into solid matrices (Gamble and Khan, 1992).
The overall mechanism can be represented by eq 1.

$$At_{solution} + S \underset{k_{S2}}{\overset{k_{B1}}{\rightleftharpoons}} AtS_{surface} \xrightarrow{k_{D1}} At_{bound} \qquad (1)$$

I. Pseudo first order kinetics for labile sorption. Based on eq 1, Gamble and Khan (1992) have expressed the overall rate for atrazine disappearance from aqueous solution as follows:

$$-\frac{dM_{At}}{dt} = k_{B1}\theta_o M_{At} - k_{S2} M_{At} \qquad (2)$$

At the very beginning, the labile sorption sites have very low loadings, so that to a good approximation one gets

$$-\frac{dM_{At}}{dt} = k_{B1}\theta_o M_{At} \qquad (3)$$

The value of k_{S2}, in eq 2, can be obtained from the weighted average equilibrium constant, K_1, given by the following equation (Gamble and Khan, 1990):

$$\bar{K}_1 = \frac{\theta_{At}}{M_{At}(\theta - \bar{\theta}_o)} = \frac{k_{B1}}{k_{S2}} \qquad (4)$$

In sufficiently long experiments the trailing edges of the filtrate and the labile curves have low slopes and become parallel to within the limit of experimental error. This indicates close approaches to labile sorption equilibrium. Two types of K_1 calculation methods can be carried out in this region of the experiments.

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(1) Extrapolation to t = ∞ days. The slurry and filtrate curves are each fitted by the method of least squares to $1/t$ day^{-1}. The intercept should represent t = ∞ days values of the moles per litre of slurry and the molarity.

(2) Averaging of curve sections. The slurry and filtrate curves are each averaged, and the averaged values are then used for the calculations in the same way as are the extrapolation values of the above method.

II. Second order kinetics for labile sorption. Gamble and Khan (1990) have pointed out that the pseudo first order kinetics for atrazine sorption is inherently less rigorously correct than the second order kinetics, especially at high active site loadings. The pseudo first order assumption confines kinetic information to the very beginning of the sorption-desorption reactions. To generate more kinetic information about sorption-desorption processes one may have to consider, not only the second order kinetics but, the overall reaction mechanism. It has been found from the HPLC-MFT that the atrazine sorption can be represented by a reaction scheme similar to that commonly used for consecutive reactions. The aqueous atrazine decreases as a function of time and that of intraparticle diffusion increases continuously. The labile atrazine concentration rises to a maximum and then decreases over time. Such behaviour for the atrazine sorption indicates that consecutive reactions are going on. Previously, the picture was not quite so clear, because the labile and non-labile sorptions have frequently not been separately determined. With the advent of the HPLC-MFT (Gamble and Khan, 1990) it is easy now to measure over time not only the rate of the overall sorption, but also the rate of labile and non-labile sorption as well. The rate law for atrazine disappearance from aqueous solution has been derived earlier (see eq 2), and that for the labile surface sorption is given by the following expression:

$$\frac{d\ddot{o}_{At}}{dt} = k_{Bl}\ddot{o}_o M_{At} - (k_{S2} + k_{Dl})\ddot{o}_{At} \qquad (5)$$

Using the steady state approximation for the labile surface sorption of atrazine the physical chemistry constants k_{B1}, k_{S2}, and k_{D1} can be immediately calculated (Cathum, et al. in preparation).

III. Apparent atrazine bound residue. Bound residues may be defined as the fraction of the total amount of pesticide, initially applied to the soil, that cannot be extracted by methods commonly used in residue analyses. When an aqueous solution of an organic chemical is brought in contact with the soil the organic chemical diffuses slowly towards the interior of the soil particle and becomes sorbed onto interior sites. The diffusion of herbicides into the soil particles can be relatively slow, depending on physicochemical properties of the soil and the herbicide. Atrazine, for instance, may take several days to diffuse inside a sediment or soil particle. This intraparticle diffusion may explain the material balance loss when a sorbed pesticide is extracted from the soil by organic solvents (Chiba, 1969). Crank (1975) gave a general case for material loss by diffusion from the plane surface of a particle into its interior. In his model, Crank assumed a steady state surface coverage for the soil particle by the

pesticide. According to Crank, the amount of material that has diffused from a plane surface initially covered with constant concentration, C_1, is expressed as follows:

$$M_t = 2C_1\sqrt{\frac{Dt}{\delta}} \qquad (6)$$

using Crank's symbols, M_t is the amount of diffused materials, C_1 is the (constant) concentration of diffusing species on the surface (g m^{-2}), D is the diffusion coefficient, t is the time. Converting grams of pesticide per square meter of surface area of adsorbing medium into moles of pesticide per gram of adsorbing medium gives $è_L$ instead of M_t as a measure of non-labile uptake. Similarly, the concentration of pesticide bound to labile sorption sites, $è_{At}$, may be used instead of C_1. If C_1 is equal to $è_{At}/\ell$, where ℓ is the particle dimension parallel to the direction of diffusion (normal to the particle surface), and M_t is equal to $è_L$ then Crank's equation may be rearranged to (Gilchrist et al., 1993)

where, $$è_L = \frac{2è_{At}}{\sqrt{\delta}}\sqrt{k_{D1}}\ t^{1/2} \qquad (7)$$

$$k_{D1} = \frac{D}{\hat{e}} \qquad (8)$$

A plot of $è_L$ versus $t^{1/2}$ will be linear with a slope.

$$Slope = \frac{2è_{At}}{\sqrt{\delta}}\sqrt{k_{D1}} \qquad (9)$$

k_{D1} is then calculated by differentiation from the slope. The steady state concentration, $è_{At}$, of the labile atrazine is measured experimentally, from the rate curves. Gamble and Ismaily (1992) have tested Crank's equation for its compliance to the above mechanism by plotting log$è_L$ vs log*t*,

$$\log(è_L) = \log\left(\frac{2è_{At}}{\delta^{1/2}}\sqrt{k_{D1}}\right) + z\log t \qquad (10)$$

and found the expected agreement between the theory and the experiment, z = 0.50. Equation 23 has been used as the basis of a diagnostic plot to test the validity of Crank's equation for behaviour consistent with the retarded intraparticle diffusion mechanism. An alternative method to be called the "Constant slope methods" described below can also be used to calculate k_{D1}.

Constant slope method. The existing literature generally assumes that the uptake by diffusion can be approximated by first order kinetics. In the present case that gives:

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The value of $d\grave{e}_L/dt$ is calculated by curve fitting at the steady state condition in the labile sorption $\frac{d\grave{e}_L}{dt} = D_f \grave{e}_{At}$ (11) coverage that is identified by plotting $\grave{e}_{At}$ versus time. Using a mean value of $\grave{e}_{At}$ over this same region of the experiment, the diffusion rate constant is calculated from eq 11. When suitable data are available, this simple and direct calculation method can give the most reliable numerical value of k_{D1}.

2 - Methodology

Bench scale laboratory test methods were created for identifying chemical processes in Great Lakes watershed soils. The parameters characterizing the processes were next measured. The HPLC-MFT method was used to generate the chemical speciation rate curves of the pesticides. This chemical information was then entered into computer models that simulate water movement in the ground. The resulting computer simulations were validated against both field and column experiments.

Identification and quantification of minerals in soils was achieved by X-ray diffraction (XRD), energy-dispersive X-ray analysis (EDXRA), and scanning electron microscopy (SEM). These three techniques were used to clarify elemental composition, shapes, sizes and crystal chemical characteristics of the soil minerals. XRD analysis was performed on powder species in random mounts for determination of the whole mineral composition and in preferred orientation for characterizing phyllosilicates. Sample preparation, diagnostic pretreatment and semi-quantification were done following a scheme described by Kodama et al. (1977). For the SEM/EDXRA analysis a small portion of the soil was impregnated with epoxy resin to prepare the thin section according to a procedure described by Guertin and Bourbeau (1971). The thin section was studied under the microscope at a range of magnification from 25 to 313 times, and described according to the terminology of Bullock (1985). Features of interest were identified in the thin section under a polarizing microscope, mounted on an SEM stub and analyzed to determine the composition of the soil. The detector tube which fits into the microscope chamber had a window at the very end which allowed X-rays to enter the detector. A Standardless Semi-Quantitative Analysis (SSQ) software package, Tracor Northern, was used to process X-ray emission spectra. For specific area measurements, the ethylene glycol monoethyl ether (EGME) by Carter et al. (1986) was used.

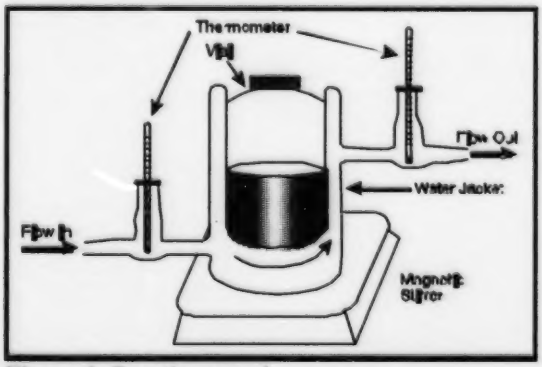

Figure 1. Reaction vessel.

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Sorption-desorption measurements. Analytical grade atrazine (99.7% purity), supplied by CIBA-GEIGY Canada Ltd. was used to prepare a stock solution of 9.997×10^{-5} M. The volumetric flask was wrapped with aluminium foil and stored in a dark place. The reaction vessel was a Pyrex cylinder, 10 cm high by 3 cm diameter, having a screw cap to prevent water loss. The soil sample and a Teflon-coated stirring bar were placed inside the vessel and stirred by a magnetic base. The reaction vessel was thermostated by connecting the doubled-walled jackets to a constant temperature bath. Figure 1 shows a schematic diagram for the reaction vessel. All kinetic analyses were carried out by use of HPLC-MFT. The microfiltrate and the whole slurry were injected separately into the HPLC, bracketed by the standard solution of atrazine (Gamble and Khan, 1990, 1992). Two stainless steel frits (2 μm and 0.5 μm) and a C18 guard column were used to trap soil particles and to protect the analytical column.

The frits, the guard column, and the analytical column prevented the soil particles from leaking into the sample cell. Hence, the measured signal was due to the unbound atrazine and not to the solid particles. The frits were removed for cleaning using ultrasonic bath after several slurry injections, or whenever the high pressure limit had been reached. The guard column was back-flashed with methanol followed by the mobile phase. A Hamilton microsyringe (0.016 inch i.d.), size 100 μL was used to inject 50 μL sample volume. A Rheodyne sample injector, Model 7125 Stainless Steel Injector and a 20 μL injection loop were used.

Atrazine sorption-desorption curves. Aqueous, labile and non-labile atrazine were determined as a function of time by use of HPLC-MFT. About 0.5 g portion of the air-dried soil was accurately weighed into a reaction vessel, stirred vigorously in 20.00 ± 0.03 mL distilled deionized water and thermostated for three days to ensure complete wetting of the soil sample. A 5.00 ± 0.01 mL aliquot of $(4.999 \pm 0.003) \times 10^{-6}$ M atrazine was then added to the reaction vessel to initiate the sorption-desorption processes. Analysis of the filtrate and the slurry began immediately with each analysis bracketed by standard atrazine solution. A small amount of the slurry (about 0.1 mL) was withdrawn with a 1 mL disposable syringe. A disposable microfilter was used to filter the slurry. The loosely bound atrazine, extracted by the mobile phase (63% methanol in water), and the free atrazine were measured. The reaction vessel was covered with a screw cap after each opening to prevent water loss by evaporation from the mouth of the vessel. Direct injection of the slurry into the HPLC caused the soil particles to deposit on the stainless steel frits and the guard column. The difference between the slurry concentration and the filtrate concentration is the concentration of the labile atrazine. The non-labile atrazine concentration was determined from the mass balance.

Determination of labile sorption capacity by sorption from solution. About 0.5 g of the air-dried soil was weighed accurately into a reaction vessel and stirred in 25 ± 0.03 mL distilled deionized water and thermostated at a predetermined temperature. Measurement of the labile surface sorption was initiated by adding a 20-μL aliquot of 0.999×10^{-4} M atrazine to the reaction vessel (seven additions per day). The method is a type of titration. Measurement of the filtrate and the slurry was done, exactly as mentioned before for the sorption-desorption curves, and continued for more than nine days to ensure complete saturation of the labile active sites. The average time for producing one datum point for the labile surface sorption after each addition was about 30 minutes. The labile sorption

capacity was then determined by plotting the labile atrazine versus aqueous atrazine remaining in solution. The labile sorption capacity determined by this method was simply site saturation at the height of the plateau.

To show the effect of soil constituents on the sorption-desorption processes the fractionated soil, <(20-2000) μm, and the non-fractionated, <2 mm, were sized down to <149 μm by gentle grinding in an agate mortar, and the labile sorption capacity was measured for both at 10.0 °C. The labile sorption capacity was measured by titrating the soil fraction with 0.999×10^{-4} M standard atrazine and the labile surface atrazine was determined as a function of aqueous atrazine remaining in solution.

3 - Findings. It has been found that the information about the physical chemistry mechanisms that influence pesticide interactions with soil integrated into the improved predictive model give better results than empirical descriptions when hydrology computer model output is checked against field measurements. The model gives more reliable estimates of bioavailable concentrations than the currently used models. Several persistence and fate mechanisms based on chemical stoichiometry by which pesticides can threaten the Great Lakes basin have been identified. The one that poses the biggest risk is the one that presents a type of bound residues. Pesticides that are trapped within the soil particles are slowly released to the environment after remediation and clean-up processes. Some of the chemical materials in the soil are found to have a profound effect on the sorption-desorption processes. Soils that contain high organic matter and clay minerals sorb the most. It is also found for the Plainfield sandy soil case that when the temperature rises the trapped herbicide atrazine diffuses out to the environment.

The test methods and the multidisciplinary model developed for the project can be used to base standards and operational guidelines on chemical species related to bioavailability and toxicity hazard, instead of simply total concentration. Multidisciplinary computer models are more reliable for risk assessment and the control of field operations than conventional single discipline models are. Cost estimates (attached) indicate that the technology developed by the project will permit a more cost effective combination of bench scale laboratory tests, computer simulations and field trials, than has been previous practice.

The new testing method should replace the currently used methods in risk assessment and regulatory work. The improved physical chemistry constants of pesticides interactions with the soil are more reliable than empirical descriptions. When making a decision to protect the environment regulatory agencies should take into account that bound pesticides can reemerge again to degrade the environment. To determine the worst case level of contaminant in the environment regulatory agencies must consider the bioavailable concentration of the pesticide and not simply the total concentration. Some of the soil particles can physically trap pesticides so that remedial action cannot easily remove them. They can subsequently be slowly released back into the environment, so that biological and health risks can persist. The time scale and the binding strength are both important factors and must be considered in solving the contamination problem.

The physical chemical properties of the soils were determined, so that their influence on the physical chemistry constants can be investigated in the future. The accumulation of such physicochemical data for various soils will eventually create a mechanisms data base that assembles soil properties and physical chemistry constants together with the geographical information. The results of the XRD analysis are given in Table I. The <20 μm fraction contained quartz (as the only major

component in association with an interstratified mineral), vermiculite, mica, microcline, plagioclase, and X-ray amorphous material which was mainly hydrous oxides and organic matter. In the <(20-2000) μm fraction, quartz was the dominant mineral. Mica, amphiboles and feldspars and calcite were present in minor amounts. Thus, the fraction <20 μm contains more phyllosilicates than <(20-2000) μm fraction. The clay minerals vermiculite and chlorite did not exist in the <(20-2000) μm fraction, they might be removed from the soil during the sedimentation process.

Mineral components of the soil were examined by the thin section. Most of the soil components, except gases and liquids can be seen in thin sections (Bullock, 1985). The soil contained coarse mineral components which included rock fragments and clay size minerals. Some colourless particles were coated with brown to very dark brown thin cutan. Crumbs and granules of aggregates of different sizes and colours, pale yellow to green, covered with a very thin cutan were seen in the soil. Some of these aggregates contained mineral grains coated with brown cutan. Also seen in the soil sample, scattered porous fibres consisting of thinly brown-coated sand grains and brown, rounded aggregates of finer material partly filling irregular spaces, and plant fragments at various stages of decomposition. There was also fine organo-mineral materials which could be living cell residues and amorphous organic material. The thin section showed varieties of colours, red, yellowish brown, brown to dark brown, grey, greenish to greyish green, and black. The red colour appeared to Zindicate the presence of fine dispersed hematite, but perhaps amorphous Fe-gels. The yellowish brown colour indicated the presence of finely dispersed, hydrated Fe-oxyhydroxides, or amorphous Fe-gels. Whereas, brown to dark brown colour mostly was due
to the presence of organic matter, commonly associated with Fe-oxyhydrates. Large amounts of humic acids were responsible for the sepia colour (brown pigment) in the thin section. The grey colour, on the other hand, indicated the presence of clay minerals and fine powdered silicates, such as, carbonate. The presence of grey colour in thin sections reflected the absence of staining substances such as Fe and organic matter. Greenish to greyish green colour indicated the presence of chlorites, which was unlikely to be due to the staining ferrous ions since ferrous ions were readily oxidized during preparation of the thin section. Fine materials, roughly, less than 10 μm, were also seen. These fine materials by far were the most important part of the soil because of the small dimension and their physical behaviour, such as the specific surface and the labile sorption capacity. The main elements Si, Al, O, K, Ca, Fe, and C were identified and quantified. Some relatively minor elements were not detected. The black spots seen in the thin section were examined carefully with
EDXRA. The result indicates that the black spots do not contain Mn, and the prominent Fe peak seen in the thin section indicates that they might be Fe-minerals (McKeague and Wang, 1980).

Table I. XRD analysis of the <20 μm and the <(20-2000) µm fractions of the Plainfield sandy soil.

Mineral	< (20-2000) µm	<20 µm
Interstratified 21 Å minerals(s) long spacing	-	*[1]
Smectite	-	-
Vermiculite	-	trace
Chlorite	-	*
Mica	*	*
Amphiboles	*	-
Quartz	****	***
Microcline	*	*
Plagioclase	*	*
Calcite	*	-
X-ray amorphous	?	Yes

Table II shows specific area values for the <149 μm and <2 mm soil fractions measured by EGME method. The results reflect the characteristic properties of the sandy soil. The specific area is an important fundamental soil property and can be used to assess physical and chemical properties of the soil. For example, a specific area of 10 m^2 g^{-1} indicates that the soil is not rich with clay minerals. Table II also presents numbers of moles of atrazine and EGME per gram of air-dried soil. As can be seen from the Table there is an appreciable difference between the surface sorption capacity of atrazine and EGME. One reason may be advanced to account for this difference. The atrazine molecules had to compete with water molecules for surface sorption sites, whereas, EGME molecules were sorbed onto dry soil particles.

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[1]Probably, Smectite, Chlorite, and/or Mica.

**** Dominant; *** Major; ** Moderate; * Minor; - Not detected.

Table II. Specific areas of the Plainfield sandy soil measured by EGME method versus atrazine labile surface sorption.

Fraction	Specific area, m^2/g	Surface sorption, Moles/g (EGME)	Surface sorption, Moles/g (Atrazine)
<149 μm (ground)	56 ± 3	(2.1 ± 0.1) x 10^{-4}	(2.1 ± 0.1) x 10^{-8}
<2 mm (non-ground)	10 ± 1	(3.7 ± 0.4) x 10^{-5}	-

Figure 2 shows a plot of labile surface sorption as a function of aqueous atrazine remaining in solution. As expected, the plot increased to a plateau that was reached as a saturation limit. The initial appearance of the plateau was observed at about $3.500x10^{-6}$ M, and its height held constant to $7.500x10^{-6}$ M indicating clearly that the fractionated soil has a very low labile sorption capacity. Whereas, the non-fractionated soil adsorbs the most. This difference in the labile sorption capacity of the <(20-2000) μm and <20 mm fraction may be attributed to the clay minerals vermiculite and chlorite, and some of the water soluble humic and organic materials which are washed out from the former during fractionation. The particle size may have no significant effect on the labile sorption capacity because the fractionated and non-fractionated soil samples were both sized down to <149 μm for HPLC measurements.

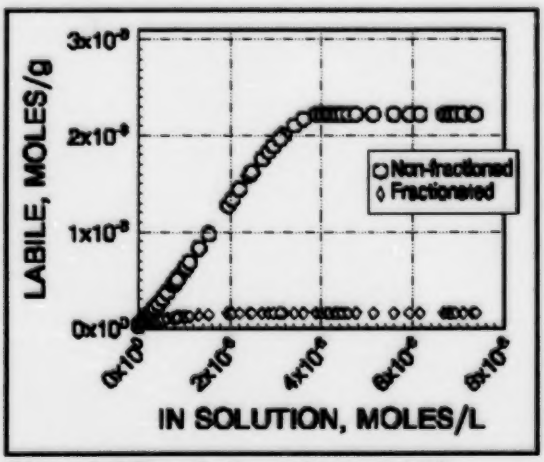

Figure 2. Effect of soil constituents on labile sorption capacity of atrazine onto Plainfield sandy soil at 10.0 °C.

Chemical speciation rate curves. long term kinetics experiments were conducted to measure over time pesticide chemical species in soils from the Great Lakes watershed at different temperatures. The result for the 10.0 °C is shown in Figure 3. As can be seen from the Figure the filtrate concentration decreased with time and then slightly levelled off after about 60 days. The labile atrazine, which is the difference between the slurry and the filtrate, increased to a maximum and then declined

after about 20 days, when intraparticle diffusion removed atrazine simultaneously from the surface sorption sites and from the solution. The diffused atrazine increased exponentially and then levelled off around 60 days indicating that the outward diffusion was becoming increasingly important as experiment proceeded. This behaviour for the sorption-desorption processes is characteristic of the consecutive reaction mechanism in which a reactant passes through a transient species and then to the product. The shapes of the experimental sorption-desorption curves indicate that a consecutive reaction mechanism does indeed exist. After 60 days of stirring at 10.0 °C the mole ratios of the atrazine species were as follows: 10% of the initial atrazine remained in solution, 5% sorbed on the surface, and 85% diffused into the soil particles, see Figure 4.

Calculation of K_1, K_D, k_{B1}, k_{S2} and k_{D1}. Table III presents a summary of the calculation at 10.0, 25.0, and 35.0 °C. The distribution coefficient, K_D, is calculated using eq 12 (Gamble and Khan, 1992)

$$K_D = \bar{K}_1 (\grave{e}_e - \grave{e}_w) \quad (12)$$

Equation 12 shows that the empirical use of K_D without any consideration of sorption capacity or site loading will cause unnecessary data scatter (Gamble and Khan, 1991). The value of k_{D1} was calculated by applying the constant slope method depicted by eq 10. An average value of $\grave{e}_{At}$, corresponding to a time interval in which the diagnostic plot of Crank's equation had yielded a value of 0.50, was used.

Table III. Summary of the physical chemistry constants of atrazine interactions with Plainfield sandy soil at different temperature calculated by the present method.

Parameter	Value[2]		
	10.0 °C	25.0 °C	35.0 °C
k_{B1}	$(9.37 \pm 0.02) \times 10^{3}$	$(6.69 \pm 0.13) \times 10^{4}$	$(6.80 \pm 0.09) \times 10^{4}$
k_{S2}	$(4.82 \pm 0.07) \times 10^{-3}$	$(3.27 \pm 0.17) \times 10^{-2}$	$(2.33 \pm 0.09) \times 10^{-2}$
k_{D1}	$(1.12 \pm 0.01) \times 10^{-2}$	$(3.56 \pm 0.11) \times 10^{-2}$	$(3.24 \pm 0.07) \times 10^{-2}$
• $_1$	$(1.94 \pm 0.03) \times 10^{6}$	$(7.40 \pm 0.42) \times 10^{6}$	$(1.35 \pm 0.05) \times 10^{6}$
K_D	$(2.46 \pm 0.07) \times 10^{-1}$	$(9.21 \pm 0.58) \times 10^{-2}$	$(6.55 \pm 0.21) \times 10^{-2}$

[2]Values after ± represent absolute standard deviation, ó.

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Figure 5 presents a typical diagnostic plot at 10.0 $_{o}$C for the Plainfield sandy soil. Two curvatures were observed in the plot, however. The first was at the very beginning of the sorption processes which may be attributed to the insignificant intraparticle diffusion, and the second appeared later when the outward diffusion became significantly important. This outward diffusion suggests that another arrow may be added to the overall sorption mechanism, depicted by eq 1, to become $At_{solution} + S \leftrightarrows AtS_{surface} \leftrightarrows At_{bound}$.

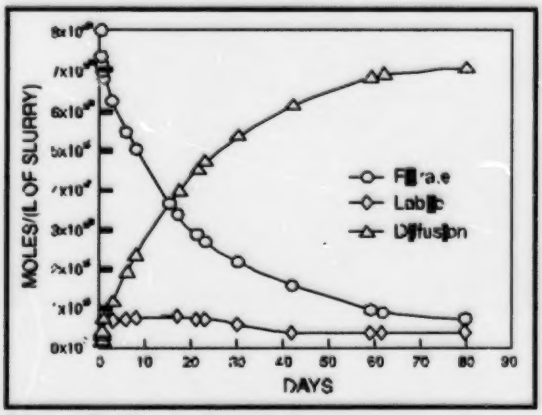

Figure 3. Chemical speciation rate curves of atrazine onto a green belt soil at 10.0°C.

The effect of temperature on atrazine intraparticle diffusion into Plainfield sandy soil particles was investigated at 10.0, 25.0, and 35.0 °C. The result is shown in Figure 6. Intraparticle diffusion is appreciably reduced as the temperature increases. The effect of temperature on the labile surface sorption capacity was also investigated and the result is shown in Figure 7. Same temperature effect is seen in the case of surface sorption of atrazine onto Plainfield sandy soil. As the temperature increased the labile surface sorption decreased.

The effect of temperature on the pesticide sorption may have an important implication for the persistence and fate mechanisms in the soil. Temperature dependence of sorption-desorption processes is not similar for all herbicides. The sorption of simazine, atrazine, and monuron by bentonite is greater at 0° C than at 50° C, while diquat is completely sorbed at both temperatures. Temperature may exert an indirect influence on sorption through its effect on the competition between pesticide molecules and water molecules for surface sorption sites. Since both sorption and vapour pressure are temperature dependent, one expects that a high pressure chemical compound favours desorption at high temperature. Since adsorption is interrelated with both temperature and bioactivity, the bioactivity of a pesticide may be different at various temperatures. Soil temperature undergoes both a seasonal variation and a diurnal change. As would be expected, the soil temperature in a temperate climate is at a minimum during the winter, increases to through spring to a maximum in the summer, and decreases in the fall. Since pesticides are generally applied to the soil in early spring when the soil temperature is in general relatively low, this would seem to favour sorption. This is beneficial from the standpoint that leaching into groundwater is greatly reduced. The temperature increases at summer reaching the

maximum in July and August thereby causing desorption of pesticides back into the environment. Strongly sorbed contaminants in winter reemerge in summer to add to the environmental contamination.

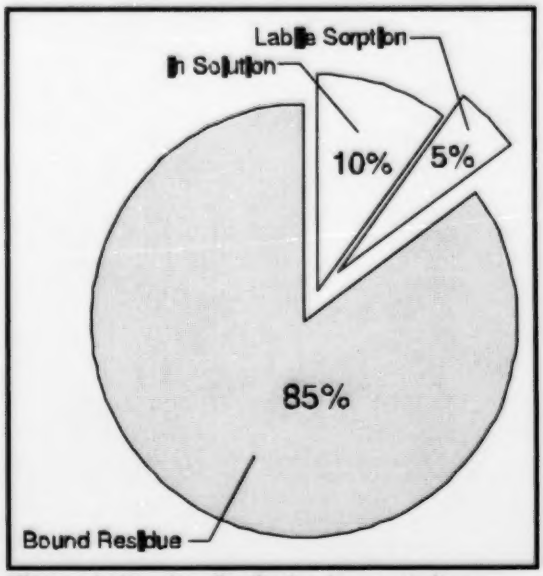

Figure 4. Atrazine distribution in a wetted green belt soil at 10.0°C. Reaction time 60 days.

Frissel (1961) has reviewed the forces involved in sorption of herbicides to clay particles. Bowman et al., 1970 have investigated the adsorptive behaviour of malathion on clay minerals. They have found that the mechanism of adsorption is through a hydrogen bonding interaction between the carbonyl group and the hydration water shells of the saturating cations. Gilchrist et al. (1993) have investigated the mechanism of atrazine interactions with clay minerals. The herbicide atrazine is less polar than water and when applied to a wetted soil only a small fraction of the total atrazine becomes sorbed. The labile surface sorption onto Plainfield sandy soil, detected by the HPLC-MFT, is due to the thin cutan that coats quartz and mineral crystals seen under the polarizing microscopy. Clean quartz crystals showing no visible coating may participate very little in the surface adsorption. The slow intraparticle diffusion may be attributed to the presence of organic matters, small cracks, and irregular foldings in the soil particles. It is believed that when atrazine is brought in contact with the Plainfield sandy soil at pH = 6.6 (the pH of the filtrate), the forces that control atrazine-soil interactions are mainly hydrogen bonding of the C=O ... cation, C=O ... H_2O ... cation, N-H ... O, and C-H ... O type. In terms of existing sorption mechanisms (Bailey and White, 1970; Weber, 1970), the atrazine may bind onto the soil particles mainly through the amino group that is attached to the benzene ring, and when applied to the soil atrazine molecules compete with water molecules for sorption. The tendency of herbicides and water toward labile active sites may vary appreciably with temperature, depending on chemical structures of herbicides, since water is common for all reacting species. Upon warming up, the molecules with the least positive enthalpy of desorption will desorb first.

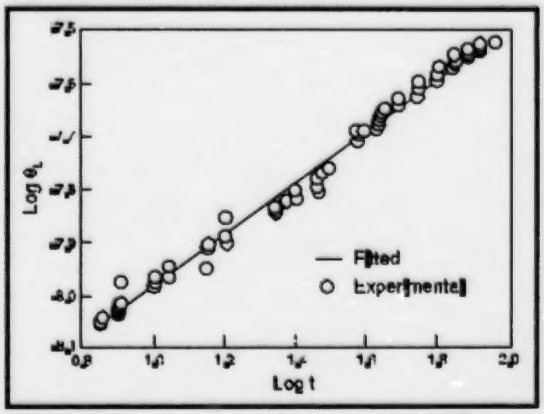

Figure 5. Diagnostic plot for intraparticle diffusion adapted from Crank's model. A Plainfield sandy soil was used. z = 0.50.

Improvement of computer simulation by the new technology. The mathematical description of equilibrium and kinetic parameters for the physical chemistry processes of pesticides in real soils have been produced (Gamble et al., 1990, 1992, 1993, 1994) and integrated into the PESTFADE, a model developed as an improvement of LEACHMP by Clemente and Prasher, 1993. Comparison of the model predictions with actual field measurements, Figure 8, over five years of intensive investigation suggest that the mathematical descriptions of real processes as described can give a substantially improved agreement of model results with actual filed data. Figure 8 presents computer simulation of atrazine movement through a soil profile. As can be seen from the Figure, excellent match between computer predictions and field measurements is obtained when Gamble's data is used as input for the computer model. This result has an important implication since it provides solid evidence that the new technology is successful in advancing environmental chemical science and technology to solve the contamination problem in the Great Lakes ecosystem.

4 - Study conclusions. The test methods and multidisciplinary model developed for the project can be used to relate standards and operational guidelines to the chemical species that influence bioavailability and toxicity hazards, instead of simply to total concentrations.Multidisciplinary computer models are more reliable for risk assessment and the control of field operations than conventional single discipline models are. Cost estimates indicate that the technology developed by the project will permit a more cost effective combination of bench scale laboratory tests, computer simulations and field trials, than has

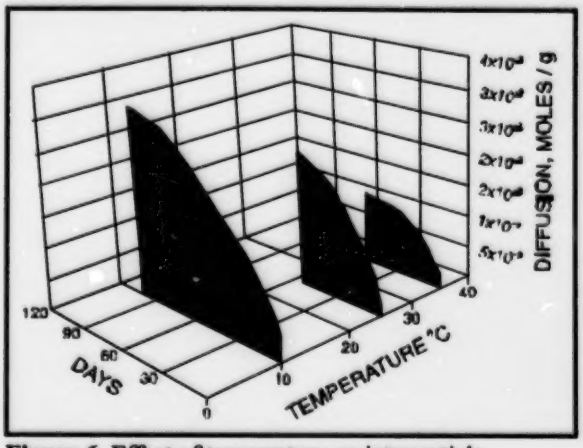

Figure 6. Effect of temperature on intraparticle diffusion of atrazine onto Plainfield sandy soil.

been previous practice. The cost estimates are attached.

The net result of the new technology is that it offers the opportunity of reducing the pesticide loading onto the Great Lakes watershed, of cutting the costs of computer model input, and of cutting the costs of crop protection.

Early validation studies indicate that this combination of new methods gives better agreement with not only laboratory column experiments, but also with filed experiments, than the conventional methods do.

We now have the opportunity to reduce the delivery of agricultural pesticides into the Great Lakes by using cheaper, faster, and more reliable methods for risk assessment and the management of field operations.

It is anticipated the future advances in soil microbiology and macropore flow research, together with

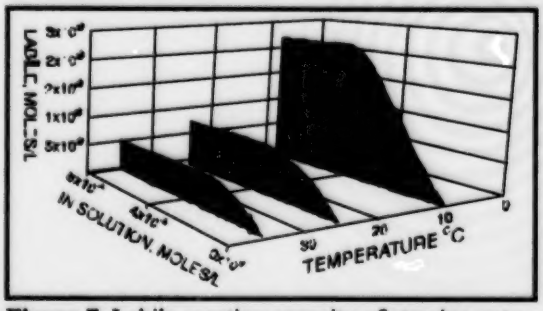

Figure 7. Labile sorption capacity of atrazine onto Plainfield sandy soil at different temperature.

an expansion of the new pesticide-soil parameter data base will make the projects' contribution even more useful.

5 - New technologies and benefits. The HPLC-MFT method is a novel technique developed in this laboratory as an experimental component of the GLWQP research. It can be used in any laboratory that has an HPLC and a constant temperature water bath. With this technology it is now possible to determine contaminant chemical species concentrations over time. This generates invaluable information about the mechanism of fate and persistence of contaminants in the environment. It can be used to complement other methods that are being used by regulatory agencies to prevent or reduce the contamination problem.

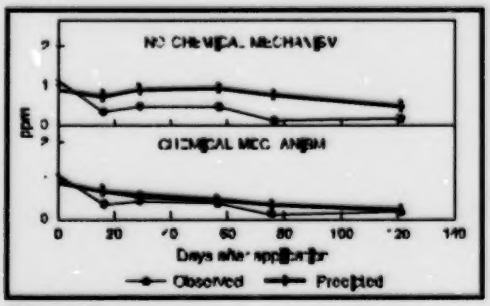

Figure 8.

6 - Implications for Great Lakes Basin ecosystem. The methods developed by the project permit the effective determination of chemical species concentrations related to risks, instead of the currently used ambiguous total concentrations. With this technology it is possible that the maximum acceptable limit of a contaminant can be determined effectively and reliably based on the chemical speciation and bound residues. The new test methods can be used in regulation and risk assessment to protect the Great Lakes ecosystem in particular and the environment in general.

7 - Technology transfer potential. It is anticipated that both the new bench scale test methods and the new type of multidisciplinary computer model can be used by commercial consulting and contracting companies, by Federal Government registration and regulatory agencies, by Provincial Government ministries, and by agricultural extension officers.

8 - Gaps/needs for future research. It is frequently pointed out that the macropore flow problem still remains unresolved, and this might limit the usefulness of the rest of the research results. The first relevant point is that some successful field and soil column validation has been obtained in spite of this. The second is that other laboratories at the University of Calgary and at the Environmental Chemistry Laboratory of the USDA-ARS in Beltsville Maryland are currently applying new NMR imaging methods to the investigation of the macropore problem. Future research should also be conducted to expand the mechanisms data base, seek trends in the effects of the types and amounts of chemical materials and the types and amounts of surfaces on the mechanisms parameters that are

used as computer model input, establish the effects of pesticide chemical structure and reactivity on the above mechanisms parameters, investigate the problems of microbiological degradation, macropores, and field variability of the above parameters, and apply and adapt the new technology to pesticide regulation, regulatory work, and practical field operations.

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APPENDIX A

HYDROLOGY MODEL INPUT: PHYSICAL CHEMISTRY INTERACTIONS OF PESTICIDES WITH SOILS FROM THE GREAT LAKES WATERSHED

Derivation of equations:

I. Labile sorption mole fractions: From Gamble and Khan (1992)

$$x_1 = \frac{\grave{e}_{At}}{\grave{e}_c} \tag{13}$$

$$\grave{e}_{At} = \grave{e}_c x_1 \tag{14}$$

$$\grave{e}_o = \grave{e}_c(1-x_1) \tag{15}$$

II. Distribution coefficient: From Gamble and Khan (1992)

$$K_D = \bar{K}_1 \grave{e}_o \tag{16}$$

$$K_D = \bar{K}_1 \grave{e}_c(1-x_1) \tag{17}$$

III. Rate constant for net loss from solution: From Gamble et al. (1990, 1992, 1993, 1994)

$$k_{Dl} = Q(\frac{D}{a}) \qquad Days^{-1} \tag{18}$$

$$Z \equiv (\frac{k_{Bl}}{\bar{K}_1} - Q\frac{D}{a})(\frac{w}{V})\grave{e}_{At} \tag{19}$$

$$\ln(k_{Dl}) = B_o + \frac{B_1}{T} \tag{20}$$

$$-(\frac{dM_{At}}{dt})_T = k_{Bl}(\frac{w}{V})\grave{e}_o M_{At} - Z \tag{21}$$

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Let

$$u \equiv \ln(k_{D1})$$

$$u \equiv B_o + \frac{B_1}{T} \tag{10}$$

$$k_{D1} = e^{u} \tag{11}$$

Equations (2), (3), and (6) are combined with equation (8) and (9).

$$Z = \left(\frac{k_{B1}}{\bar{K}_1} - k_{D1}\right)\left(\frac{w}{V}\right)x_1 - R_{D2} \tag{12}$$

From the hydrology models,

$$-\left(\frac{dM_{At}}{dt}\right)_T = k_{B1}\left(\frac{w}{V}\right)\grave{e}_c(1-x_1)M_{At} - Z \tag{13}$$

$$-\left(\frac{dM_{At}}{dt}\right)_T = kM_{At} \tag{14}$$

Equations (12) to (14) are combined to give equation (15).

$$kM_{At} = k_{B1}\left(\frac{w}{V}\right)(1-x_1)M_{At} - \left(\frac{k_{B1}}{\bar{K}_1} - k_{D1}\right)\left(\frac{w}{V}\right)\grave{e}_c x_1 + R_{D2} \tag{15}$$

$$kM_{At} = \left(\frac{w}{V}\right)\grave{e}_c\left[k_{B1}(1-x_1)M_{At} - \left(\frac{k_{B1}}{\bar{K}_1} - k_{D1}\right)X_1 + \frac{R_{D2}}{\left(\frac{w}{V}\right)\grave{e}_c}\right] \tag{16}$$

$$kM_{At} = \left(\frac{w}{V}\right)\grave{e}_c\left[k_{B1}M_{At} - k_{B1}M_{At}X_1 - \left(\frac{k_{B1}}{\bar{K}_1} - k_{D1}\right)X_1 + \frac{R_{D2}}{\left(\frac{w}{V}\right)\grave{e}_c}\right] \tag{17}$$

$$kM_{At} = \left(\frac{w}{V}\right)\grave{e}_c\left[k_{B1}M_{At} - \left(k_{B1}M_{At} + \frac{k_{B1}}{\bar{K}_1} + k_{D1}\right)x_1 + \frac{R_{D2}}{\left(\frac{w}{V}\right)\grave{e}_c}\right] \tag{18}$$

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$$k = (\frac{w}{V})\grave{e}_c[k_{B1} - (k_{B1} + \frac{k_{B1}}{\bar{K}_1 M_{At}} + \frac{k_{D1}}{M_{At}})x_1 + \frac{R_{D2}}{(\frac{w}{V})\grave{e}_c M_{At}}] \quad (19)$$

It is convenient to define two parameters, K_2 and K_3 as follows,

$$K_2 \equiv (k_{B1} + \frac{k_{B1}}{\bar{K}_1 M_{At}} + \frac{k_{D1}}{M_{At}})x_1 \quad (20)$$

$$K_3 \equiv \frac{R_{D2}}{(\frac{w}{V})\grave{e}_c M_{At}} \quad (21)$$

The hydrology rate parameter k is therefore not a constant, but is instead a function $f(X_1, M_{At}, T)$ that is described by equations (15), (20), (21), and (22).

$$k = (\frac{w}{V})\grave{e}_c(K_{B1} - K_2 + K_3) \quad (22)$$

NOTES FOR THE HYDROLOGY MODEL INPUT:

1. The equations accounts for labile sorption, labile desorption, and intraparticle diffusion in terms of equilibria and kinetics.
2. The temperature dependence of the labile sorption and intraparticle diffusion is accounted for over the range 15.0 °C to 35.0 °C.
3. K_D is not inherently a constant and under some conditions might vary over a significant range. If however, the labile sorption is sufficiently small or covers a very small range, then the changes in it might become small compared to experimental error.
4. K_D is seen to depend on the labile sorption capacity.

5. The model rate parameter k is not a constant. In addition to being a function of labile sorption site coverage, solution concentration, and temperature, its numerical value depends directly on both the labile sorption capacity and the ratio of soil to solution. Any neglect of these factors will cause unnecessary data scatter and loss of predictive capability.
6. At the very beginning of the sorption process when the labile sorption is still very small and the diffusional uptake is still zero, K_3 will be zero, K_2 will be very small, and k_{B1} will dominate the properties of k. The result will be an early surge of atrazine out of the solution onto the labile sorption sites. This will make K_2 relatively more important while K_3 is still very small. The result will be a surge of atrazine off the labile sorption sites into the intraparticle diffusion process. This tends to deplete the reservoir of atrazine on the labile sorption sites. These consecutive processes are simple mass action effects, controlled by rate constants and concentration gradients.
7. It can be seen in the equations that it is essential to measure the labile sorption capacity and enter it into the calculations. Otherwise, there will be confusing errors and loss of predictive capability. Note that the capacity is defined and measured as a saturation limit. Any neglect of the soil to solution ratio will cause comparable difficulties. The fundamental reason is that both the labile sorption capacity and the soil to solution ratio are the necessary means by which the law of mass action would leave a fundamental flaw in the operation of the hydrology model. This is one of the main reasons why empirical data fail to properly support predictions.
8. Under many circumstances the reverse diffusion rate R_{D2} will be small, but under other conditions it could become important. Three important experiments have been completed at 10.0 °C, 25.0 °C, and 35.0 °C. The physical chemistry constants that control atrazine interactions with the soil have been calculated at each temperature.

Table 1. **Subroutine equations for the physical chemistry interactions of atrazine with Plainfield sandy soil (Bruce Bowman, London Research Centre).**

No.	Atrazine-Plainfield sandy soil interaction equation	Value			Units of dependent variable
		10 °C	25 °C	35 °C	
1	$x_1 = \grave{e}_{At} / \grave{e}_c$	0.333	0.443	0.523	Mole fraction
	$T = 273.16 + t$	283.16	298.16	308.16	°K
5	$K_D = \overline{K_1}\, \grave{e}_c\, (1 - x_1)$	0.149	0.0605	0.0350	(L/g)
10	$u = B_o + B_1/T$	-7.911	-6.262	-6.632	Dimensionless Ln units
11	$k_{D1} = e^u$	3.668×10^{-4}	1.908×10^{-3}	1.317×10^{-3}	$Days^{-1}$
20	$K_2 = (k_{B1} + \frac{k_{B1}}{\overline{K_1} M_{At}} + \frac{k_{D1}}{M_{At}})\, x_1$	8.147×10^4	7.390×10^6	2.434×10^5	(g/MolesxDays)
21	$K_3 = R_{D2} / (w/V)\, \grave{e}_c\, M_{At}$	-	-	-	(g/MolesxDays)
22	$k = (w/V)\, \grave{e}_c\, (k_{B1} - K_2 + K_3)$	-	-	-	$Days^{-1}$

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Table 2. Constants for subroutines.

Type of constant	Experimental value			Units
	10 °C	25 °C	35 °C	
$è_c$	2.22×10^{-8}	8.51×10^{-9}	5.30×10^{-9}	Moles/g
K_1	5.31×10^{5}	6.11×10^{5}	6.34×10^{5}	M^{-1}
B_0	-	-	-	Dimensionless
B_1	-	-	-	°K
k_{B1}	5.409×10^{4}	4.834×10^{5}	1.829×10^{5}	(g/MolesxDays)
(w/V)	20	20	20	(g/L)

Table 3. Variables for subroutines.

Type of Variable	Experimental value			Units
	10 °C	25 °C	35 °C	
$è_{At}$	7.50×10^{-9}	3.33×10^{-9}	2.61×10^{-9}	(Moles/g)
t	10	25	35	°C
M_{At}	5.750×10^{-7}	5.497×10^{-7}	7.700×10^{-7}	(Moles/L)
R_{D2}	-	-	-	(Moles/L)/Day

Table 4. Subroutine input into hydrology models.

Model parameter	Mathematical functions supplied as data points for curves
Distribution function	$K_D = f_1 (X_1)$
Rate constant for loss from solution	$k = f_2 (X_1, M_{At}, T)$

APPENDIX B

COST ESTIMATES OF PRODUCING INPUT FOR PESTICIDE COMPUTER MODELS

(I) **HPLC-microfiltration: Bench scale laboratory test method**: Total elapsed work time, about two (2) months.

COSTS:

- supervising chemist, at the rate of 0.1 PY	
0.1 x (1/6) x $70,000	$1,116.67
- technician, at the rate of 0.7 PY	
0.7 x (1/6) x $35,000	$4,083.33
- chemicals, supplies, laboratory overhead	
(1/6) x $20,000	$3,333.33
- data processing, interpretation and reporting	$2,000.00
TOTAL	**$10,533.33**

(II) **Field Experiments:** Total elapsed time, 5 months for each of three (3) summers.

COSTS:

- agronomist, at the rate of 0.2 PY	
0.2 x (15/12) x $70,000	$17,500.00
- soil scientist, at the rate of 0.2 PY	
0.2 x (15/12) x $70,000	$17,500.00
- technician, at the rate of 0.7 PY	
0.7 x (15/12) x $35,000	$30,000.00
- two (2) field hands, each at the rate of 0.5 PY	
2 x 0.5 x (15/12) x $25,000	$31,235.00
- tractor, $200/month	
15 x $200	$3,000.00
- truck, $300/month	
15 x $300	$4,500.00
- analytical chemical services	$10,000.00
- materials and supplies	$15,000.00
- data processing and reporting	$2,000.00
TOTAL	**$131,375.00**

(III) Conclusions:

The present heavy dependence on field experiments should be replaced by an optimum combination of bench scale experiments and field experiments.